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van Faassen, M.; de Boeij, P. L.; van Leeuwen, R.; Berger, J. A.; Snijders, J. G.

Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.1529679](https://doi.org/10.1063/1.1529679)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2003

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

van Faassen, M., de Boeij, P. L., van Leeuwen, R., Berger, J. A., & Snijders, J. G. (2003). Application of time-dependent current-density-functional theory to nonlocal exchange-correlation effects in polymers. *Journal of Chemical Physics*, 118(3), 1044-1053. <https://doi.org/10.1063/1.1529679>

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Application of time-dependent current-density-functional theory to nonlocal exchange-correlation effects in polymers

M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger, and J. G. Snijders

Theoretical Chemistry, Materials Science Centre, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 1 August 2002; accepted 24 October 2002)

We provide a successful approach towards the solution of the longstanding problem of the large overestimation of the static polarizability of conjugated oligomers obtained using the local density approximation within density-functional theory. The local approximation is unable to describe the highly nonlocal exchange and correlation effects found in these quasi-one-dimensional systems. Time-dependent current-density-functional theory enables us to describe ultranlocal exchange-correlation effects within a local current description. Recently a brief account was given of the application of the Vignale–Kohn current-functional [G. Vignale and W. Kohn, *Phys. Rev. Lett.* **77**, 2037 (1996)] to the axial polarizability of oligomer chains [M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger, and J. G. Snijders, *Phys. Rev. Lett.* **88**, 186401 (2002)]. With the exception of the model hydrogen chain, our results were in excellent agreement with best available wavefunction methods. In the present work we further outline the underlying theory and describe how the Vignale–Kohn functional was implemented. We elaborate on earlier results and present new results for the oligomers of polyethylene, polysilane, polysilene, polymethineimine, and polybutatriene. The adiabatic local density approximation gave good results for polyethylene, which were slightly modified by the Vignale–Kohn functional. In all other cases the Vignale–Kohn functional gave large improvements upon the adiabatic local density approximation. The Vignale–Kohn results were in agreement with best available data from wave function methods. We further analyze the hydrogen chain model for different bond length alternations. In all these cases the Vignale–Kohn correction upon the adiabatic local density approximation was too small. Arguments are given that further improvements of the functional are needed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1529679]

I. INTRODUCTION

Time-dependent density-functional theory (TDDFT) is a promising method that can handle large systems and is competitive in accuracy with other methods.^{1–3} So far TDDFT has been applied mainly within the adiabatic local density approximation (ALDA) in which the exchange-correlation (xc) potential v_{xc} is simply a local functional of the electron density. However, this approximation was shown to fail dramatically for the case of long molecular chains. For this case large overestimations of the polarizabilities and hyperpolarizabilities have been observed.^{4–6} The reason of the failure of the ALDA is precisely its locality. In this approximation the potential depends only on the local density. Therefore the potential in the center of the molecular chain is insensitive to changes in the charges at the endpoints of the chain. For the exact exchange-correlation potential, however, these endpoint charges turn out to have important global effects. In particular it gives rise to a counteracting xc-field, i.e., an xc-potential that increases linearly along the molecular chain.^{5,7,8} The induced density does not show an increase along the chain. Therefore such a counteracting term cannot be reproduced by a simple local approximation for v_{xc} , which causes the overestimation of the polarizability by the ALDA. To obtain such global changes in v_{xc} as a functional of the electron density, the functional must be nonlocal.⁹

Nonlocal density functionals that do describe the counteracting field are, for example, the exchange-only Krieger–Li–Iafrate (KLI)¹⁰ approximation and the common energy denominator approximation (CEDA).^{11,12} The orbital dependent KLI potential already improves the polarizability of the much discussed hydrogen chain model H_{2n} (see, for example, Refs. 13, 14, and references therein) compared to the local density approximation (LDA) and generalized gradient approximations (GGAs).^{5,11} The CEDA is based on the common energy denominator approximation for the static orbital Green's function. The polarizabilities obtained for the hydrogen chain model using the CEDA improve the KLI results.¹¹ Basis of the success of these exchange-only potentials is their explicit dependence on the orbitals, which allows for a nonlocal dependence on the density. Currently these approaches are restricted to the exchange-only approximation on one hand, and on the other hand by the fact that they can only treat longitudinal fields.

Another way to include nonlocality, which, in addition, allows for transverse external fields, is by the use of current functionals. The current \mathbf{j} can be used as a local indicator of global changes in the system. This is essential for the calculation of the macroscopic polarization of solids,^{15–18} which is impossible to obtain from an infinite system calculation based on pure density functional theory.^{9,19–21} The variable

conjugate to the current density is the vector potential, in analogy with the scalar potential being conjugate to the electron density. In the Kohn–Sham approach to time-dependent current-density functional theory (TDCDFT) this vector potential also has an xc-component \mathbf{A}_{xc} . This xc-vector potential is needed to satisfy the constraint that not only the true density is obtained in the noninteracting Kohn–Sham system, but now also the true current density. The longitudinal part of the current is completely determined by the density through the continuity equation. Therefore \mathbf{A}_{xc} is needed to fix the transverse part of the current. Once an approximation is given for \mathbf{A}_{xc} , the Kohn–Sham equations can be solved self-consistently. However, few approximations are known. Vignale and Kohn (VK) were the first to propose such an approximation.^{22,23} Their motivation was to develop an xc-functional that is nonlocal in time, but still local in space. It was found that nonlocality in time implies ultranonlocality in space, if one insists on using the density as the basic variable. However, a dynamical xc-functional that is nonlocal in time but local in space, can be constructed in terms of the current density. They did a careful analysis of the weakly inhomogeneous electron gas and arrived at an expression^{22–25} for the induced xc-electric field. This expression has already been applied successfully to plasmon linewidths in quantum wells^{26,27} and in simplified form to calculate optical spectra of solids.²⁸

In a previous study we showed that the VK functional proved to be very successful for the calculation of the polarizability for a number of conjugated oligomers.⁶ In the same work some arguments were given for the applicability of the VK functional to these systems. A much smaller improvement was obtained for the hydrogen chain model. In this work we will extend our study and investigate the performance of this functional by calculating the axial polarizability for various other oligomers.

The main question that remained unanswered in previous work is why the VK functional for the model hydrogen chain gave such a small correction to the ALDA. In contrast, the corrections for the π -conjugated oligomers were large and in agreement with best available wave function methods. This may suggest that the VK functional only performs well for π -conjugated systems. In a conjugated system the induced current is carried by the π -bonds that are delocalized over the entire molecule. In hydrogen, on the other hand, the dominant contributions arise from polarized σ -bonds within the H_2 units. For the two types of systems the functional therefore probes different density regions. To investigate this point further we will study several additional systems that are either nonconjugated (polyethylene), σ -conjugated (polysilane), or π -conjugated oligomers (polymethineimine, polysilene, and polybutatriene).

II. THEORY

Time-dependent density-functional-theory is based on the theorem by Runge and Gross¹ which states that for a finite system and a given initial state a one-to-one correspondence exists between the time dependent external scalar potential $v(\mathbf{r}, t)$ (modulo a purely time-dependent function) and the time-dependent density $\rho(\mathbf{r}, t)$. Under a v -represent-

ability assumption they have shown that the time-dependent Kohn–Sham equations can be derived for a system of independent particles in an effective potential $v_{\text{eff}}(\mathbf{r}, t)$,

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}, t) \right] \psi_k(\mathbf{r}, t) = i \frac{\partial}{\partial t} \psi_k(\mathbf{r}, t). \quad (1)$$

Ghosh and Dhara^{29,30} adapted the time-dependent density-functional formalism to many-electron systems subjected to external electromagnetic fields with arbitrary time-dependence. They showed that, for a given initial state, the single-particle current density $\mathbf{j}(\mathbf{r}, t)$ uniquely determines the external scalar potential $v(\mathbf{r}, t)$ and vector potential $\mathbf{A}(\mathbf{r}, t)$ up to an arbitrary gauge transformation.³¹ Within this extended formalism the time-dependent Kohn–Sham equations, Eq. (1), become

$$\left(\frac{1}{2} [-i\nabla + \mathbf{A}_{\text{eff}}(\mathbf{r}, t)]^2 + v_{\text{eff}}(\mathbf{r}, t) \right) \psi_k(\mathbf{r}, t) = i \frac{\partial}{\partial t} \psi_k(\mathbf{r}, t). \quad (2)$$

The time-dependent effective potentials $v_{\text{eff}}(\mathbf{r}, t)$ and $\mathbf{A}_{\text{eff}}(\mathbf{r}, t)$ are uniquely determined by the exact time-dependent density and current density. These densities can be obtained from the orbitals of Eq. (2), $\psi_k(\mathbf{r}, t)$, by,

$$\rho(\mathbf{r}, t) = \sum_k f_k \psi_k^*(\mathbf{r}, t) \psi_k(\mathbf{r}, t) \quad (3)$$

and

$$\mathbf{j}(\mathbf{r}, t) = \sum_k f_k \frac{-i}{2} [\psi_k^*(\mathbf{r}, t) \nabla \psi_k(\mathbf{r}, t) - \psi_k(\mathbf{r}, t) \nabla \psi_k^*(\mathbf{r}, t)] + \rho(\mathbf{r}, t) \mathbf{A}_{\text{eff}}(\mathbf{r}, t). \quad (4)$$

Here f_k are the occupation numbers, which for the spin-restricted case are 2 for the occupied states and 0 for the unoccupied states. Equation (4) denotes the physical current density, that is, the sum of the diamagnetic and paramagnetic contributions. This physical current density is gauge invariant. For purely longitudinal vector potentials (which can be gauge transformed into scalar potentials), the density calculated from Eq. (3) is identical to that calculated from the time-dependent Kohn–Sham equations of pure density functional theory.

We want to calculate the response of our system, initially in the ground state, to an externally applied electric field. Since we use linear response theory, it will be convenient to work in the frequency domain from now on. The Fourier transform is given by

$$\mathbf{A}(t) = \int \mathbf{A}(\omega) e^{-i\omega t} d\omega. \quad (5)$$

We will only consider induced quantities to first order in the external field. For the induced effective scalar and vector potentials we choose the following form:

$$\delta v_{\text{eff}}(\mathbf{r}, \omega) = \delta v_H(\mathbf{r}, \omega) + \delta v_{\text{xc}}(\mathbf{r}, \omega), \quad (6)$$

$$\delta \mathbf{A}_{\text{eff}}(\mathbf{r}, \omega) = -\frac{i}{\omega} \mathbf{E}_{\text{ext}}(\mathbf{r}, \omega) + \delta \mathbf{A}_{\text{xc}}(\mathbf{r}, \omega), \quad (7)$$

where $\delta v_H(\mathbf{r}, \omega)$ represents the first order change in the Hartree potential and $\delta v_{xc}(\mathbf{r}, \omega)$ the first order change in the scalar xc-potential. Here $\mathbf{E}_{\text{ext}}(\mathbf{r}, \omega) = i\omega \mathbf{A}_{\text{ext}}(\mathbf{r}, \omega)$ is the applied external electric field and $\delta \mathbf{A}_{xc}(\mathbf{r}, \omega)$ is the xc-vector potential. Of course all scalar potentials can be absorbed into the longitudinal part of the vector potential by a simple gauge transformation.^{22,23} However, our choice has the advantage that in the case $\mathbf{A}_{xc} = 0$ our approach reduces to the standard TDDFT approach. The first order xc-contributions have the general form,

$$\delta v_{xc}(\mathbf{r}, \omega) = \int f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \delta \rho(\mathbf{r}', \omega) d\mathbf{r}', \quad (8)$$

$$\delta \mathbf{A}_{xc,i}(\mathbf{r}, \omega) = \sum_k \int f_{xc,ik}(\mathbf{r}, \mathbf{r}', \omega) \delta \mathbf{j}_k(\mathbf{r}', \omega) d\mathbf{r}'. \quad (9)$$

These equations define the $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ and $f_{xc,ik}(\mathbf{r}, \mathbf{r}', \omega)$ xc-kernels. For the homogeneous electron gas, $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ and $f_{xc,ik}(\mathbf{r}, \mathbf{r}', \omega)$ merely depend on the separation $|\mathbf{r} - \mathbf{r}'|$. If we Fourier transform $f_{xc,ik}(\mathbf{r}, \mathbf{r}', \omega)$ with respect to $\mathbf{r} - \mathbf{r}'$ one arrives at the following form:

$$f_{xc,ij}(k, \omega) = \frac{1}{\omega^2} [f_{xcL}(k, \omega) k_i k_j + f_{xcT}(k, \omega) (k^2 \delta_{ij} - k_i k_j)]. \quad (10)$$

This defines the longitudinal and transverse xc-kernels $f_{xcL}(k, \omega)$ and $f_{xcT}(k, \omega)$.

In the original TDDFT formulation, a formally exact representation of the linear density response of an interacting many-electron system can be derived in terms of the response function of the corresponding noninteracting Kohn–Sham system and an xc-kernel.³² This derivation can be extended to time-dependent current-density functional theory. In this case the induced density and the induced current-density are obtained from

$$\delta \rho(\mathbf{r}, \omega) = \int (\chi_{\rho j}^s(\mathbf{r}, \mathbf{r}', \omega) \cdot \delta \mathbf{A}_{\text{eff}}(\mathbf{r}', \omega) + \chi_{\rho \rho}^s(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{eff}}(\mathbf{r}', \omega)) d\mathbf{r}', \quad (11)$$

$$\delta \mathbf{j}(\mathbf{r}, \omega) = \int (\{\chi_{jj}^s(\mathbf{r}, \mathbf{r}', \omega) - \chi_{jj}^s(\mathbf{r}, \mathbf{r}', 0)\} \cdot \delta \mathbf{A}_{\text{eff}}(\mathbf{r}', \omega) + \chi_{jp}^s(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{eff}}(\mathbf{r}', \omega)) d\mathbf{r}', \quad (12)$$

where the effective potentials are given by Eq. (7). Equation (12) gives an expression for the total induced current, containing the paramagnetic and diamagnetic term. The diamagnetic term was included using the conductivity sum rule,

$$[\chi_{jj}^s(\mathbf{r}, \mathbf{r}', 0)]_{ij} + \rho_0(\mathbf{r}) \delta_{ij} \delta(\mathbf{r} - \mathbf{r}') = 0. \quad (13)$$

The Kohn–Sham response functions can be expressed in terms of the unperturbed Kohn–Sham orbitals $\phi_n(\mathbf{r})$,

$$\chi_{ab}^s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{n,n'} (f_n - f_{n'}) \times \frac{\phi_n^*(\mathbf{r}) \hat{a} \phi_{n'}(\mathbf{r}) \phi_{n'}^*(\mathbf{r}') \hat{b} \phi_n(\mathbf{r}')}{(\epsilon_n - \epsilon_{n'}) + \omega + i\eta}. \quad (14)$$

In this equation the density operator $\hat{\rho} = 1$ and the paramagnetic current operator $\hat{\mathbf{j}} = -i(\nabla - \nabla^\dagger)/2$ can be substituted for the operators \hat{a} and \hat{b} , ϵ_n are the Kohn–Sham eigenvalues, and f_n are the occupation numbers of the Kohn–Sham orbitals. The infinitesimal η ensures that the response function has the correct causal (retarded) structure. Once an approximation for the xc-potentials $v_{xc}(\mathbf{r}, \omega)$ and $\mathbf{A}_{xc}(\mathbf{r}, \omega)$ [or the xc kernels $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ and $f_{xc,ik}(\mathbf{r}, \mathbf{r}', \omega)$] is known in terms of the density and current, Eqs. (11) and (12) can be solved self-consistently.

The property we want to obtain in this paper is the linear polarizability. When a molecule is placed in an electric field it acquires an induced dipole moment given by the following relationship:

$$\delta \mu(\omega) = - \int \mathbf{r} \delta \rho(\mathbf{r}, \omega) d\mathbf{r}. \quad (15)$$

Using the continuity equation we can write the induced dipole moment in terms of the induced current density,

$$\delta \mu(\omega) = \frac{i}{\omega} \int \delta \mathbf{j}(\mathbf{r}, \omega) d\mathbf{r}. \quad (16)$$

In linear response the dipole moment and the polarizability are related by

$$\mu_i(\omega) = \mu_i^{(0)} \delta(\omega) + \sum_j \alpha_{ij}(\omega) E_{\text{ext},j}(\omega), \quad (17)$$

where $\mu^{(0)}$ is the static dipole moment, and $\alpha_{ij}(\omega)$ are the elements of the polarizability tensor. From Eq. (16) we see that the polarizability tensor can be calculated once we have obtained $\delta \mathbf{j}(\mathbf{r}, \omega)$ for a given external field $\mathbf{E}_{\text{ext}}(\omega)$. The static polarizability can be obtained by taking the limit $\omega \rightarrow 0$.

The general structure of TDCDFT has been explained. We now consider a particular form for the xc-current functional derived by Vignale and Kohn. They considered an electron gas in a periodic perturbing potential with wave vector q . The VK-functional was derived by an expansion to second order in wave vectors k and q , which characterize the Fourier component of the current–current response function and the wavelength of the inhomogeneity, respectively. Since the expansion was carried out to second order, we only need second derivatives of the current in real space. This expansion was shown to be valid in the regime $k, q \ll k_F$, ω/v_F , where k_F and v_F are the Fermi momentum and velocity. This is the region above the particle–hole continuum. The VK-functional satisfies two important constraints which are valid for systems with arbitrary time-dependence and inhomogeneity (such as molecules in external fields), stating that in linear response the xc-electric field does not exert any forces or torques on the system. Another exact property, which is satisfied for any system, is that under rigid translation of the center of mass, described by position vector $\mathbf{x}(\omega)$ also the xc-potential is translated over this vector. This immediately implies that the VK-functional satisfies the so-called harmonic potential theorem.^{33,34}

It has been shown by Vignale, Ullrich, and Conti^{24,27} that the VK expression can be written in the form of a viscoelastic field,

$$\delta \mathbf{E}_{xc}(\mathbf{r}, \omega) = \nabla \delta v_{xc}^{ALDA}(\mathbf{r}, \omega) + i\omega \delta \mathbf{A}_{xc}^{viscoel}(\mathbf{r}, \omega), \quad (18)$$

$$\delta A_{xc,i}^{viscoel}(\mathbf{r}, \omega) = \frac{i}{\omega \rho_0(\mathbf{r})} \sum_j \partial_j \sigma_{xc,ij}(\mathbf{r}, \omega). \quad (19)$$

The VK expression gives a relation between first order quantities only. In fact this expression is an approximation for the $f_{xc,ik}(\mathbf{r}, \mathbf{r}', \omega)$ kernel from Eq. (9). The VK functional is to be used in conjunction with the local density approximation for the ground-state calculation. The scalar potential is given in the adiabatic local density approximation (ALDA) by

$$v_{xc}^{ALDA}[\rho](\mathbf{r}, \omega) = \frac{de_{xc}}{d\rho}(\rho(\mathbf{r}, \omega)), \quad (20)$$

in which $e_{xc}(\rho)$ is the exchange-correlation energy per unit volume of the homogeneous electron gas. The tensor $\sigma_{xc}(\mathbf{r}, \omega)$ has the structure of a viscoelastic stress tensor,

$$\begin{aligned} \sigma_{xc,ij}(\mathbf{r}, \omega) = & \tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega) [\partial_j u_i(\mathbf{r}, \omega) + \partial_i u_j(\mathbf{r}, \omega) \\ & - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{u}(\mathbf{r}, \omega)] \\ & + \tilde{\zeta}_{xc}(\rho_0(\mathbf{r}), \omega) \delta_{ij} \nabla \cdot \mathbf{u}(\mathbf{r}, \omega). \end{aligned} \quad (21)$$

In this expression $\mathbf{u}(\mathbf{r}, \omega) = \delta \mathbf{j}(\mathbf{r}, \omega) / \rho_0(\mathbf{r})$ is the velocity field, in which $\delta \mathbf{j}(\mathbf{r}, \omega)$ is the induced current density and $\rho_0(\mathbf{r})$ is the ground state density. The coefficients $\tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega)$ and $\tilde{\zeta}_{xc}(\rho_0(\mathbf{r}), \omega)$ are frequency dependent functions of the ground state density and represent complex bulk and shear viscosities. They are determined by the $k \rightarrow 0$ limit of the longitudinal and transverse response kernels $f_{xcL}(k, \omega)$ and $f_{xcT}(k, \omega)$ of the homogeneous electron gas of Eq. (10),

$$f_{xcL(T)}(\omega) = \lim_{k \rightarrow 0} f_{xcL(T)}(k, \omega). \quad (22)$$

Approximate response kernels are known in this limit.^{35–39} We have²⁴

$$\tilde{\eta}_{xc}(\omega) = -\frac{\rho_0^2}{i\omega} f_{xcT}(\omega), \quad (23)$$

$$\tilde{\zeta}_{xc}(\omega) = -\frac{\rho_0^2}{i\omega} \left(f_{xcL}(\omega) - \frac{4}{3} f_{xcT}(\omega) - \frac{d^2 \epsilon_{xc}}{d\rho_0^2} \right), \quad (24)$$

where $\epsilon_{xc}(\rho_0)$ is the xc-energy per unit volume of the homogeneous electron gas of density ρ_0 . The transverse kernel appears because in general we will not only have longitudinal currents but also transverse ones. Equation (21) is analogous to an expression that describes forces in an elastic medium, in which case \mathbf{u} is a displacement field.

Vignale, Ullrich, and Conti²⁴ have shown that $\omega \tilde{\zeta}_{xc}(\omega)$ vanishes in the limit $\omega \rightarrow 0$, whereas only the imaginary part of $\omega \tilde{\eta}_{xc}(\omega)$ remains finite in this limit. The strange fact that the shear modulus does not vanish in the limit of $\omega \rightarrow 0$ (unlike in ordinary liquids) comes ultimately from the fact that the limit $k \rightarrow 0$ [see Eq. (22)] is taken before the limit $\omega \rightarrow 0$ (i.e., above the particle hole continuum). Thus the system remains “dynamical” down to zero frequency. By contrast, the bulk modulus is already entirely accounted for by the ALDA.

III. IMPLEMENTATION

We have implemented the current-response theory outlined in the previous section in the Amsterdam density-functional program package (ADF).^{40–45} Our implementation is analogous to the implementation of TDDFT response theory by van Gisbergen, Snijders, and Baerends.⁴⁶ The most important new feature is the way in which the matrix elements of the xc-field need to be evaluated. By combining Eqs. (11) and (12) with Eq. (14) we see that we only need to calculate the matrix elements between the Kohn–Sham orbitals and the perturbation to obtain the induced density and the induced current-density. In turn these densities are used to update the approximations for the effective potentials using Eqs. (6) and (7). We choose a gauge in which the ALDA contribution is part of the scalar potential. The matrix elements of the remaining contribution can be expressed as

$$H_{ia}(\omega) = -\langle \phi_a | \frac{1}{2} (\hat{\mathbf{j}} \cdot \mathbf{A}_{xc}^{viscoel}(\mathbf{r}, \omega) + \mathbf{A}_{xc}^{viscoel}(\mathbf{r}, \omega) \cdot \hat{\mathbf{j}}) | \phi_i \rangle \quad (25)$$

with $\hat{\mathbf{j}} = -i(\nabla - \nabla^\dagger)/2$, where ∇^\dagger acts on all terms to the left.

In order to evaluate Eq. (25) it is convenient to define the velocity field elements \mathbf{v} as

$$\mathbf{v}_{ia}(\mathbf{r}) = \frac{\mathbf{j}_{ia}(\mathbf{r})}{\rho_0(\mathbf{r})}, \quad (26)$$

where the transition current elements are defined as,

$$\mathbf{j}_{ia}(\mathbf{r}) = \frac{-i}{2} (\phi_a^*(\mathbf{r}) \nabla \phi_i(\mathbf{r}) - \phi_i(\mathbf{r}) \nabla \phi_a^*(\mathbf{r})). \quad (27)$$

Using some vector identities, integration by parts and the fact that total differentials integrate to zero due to Gauss’ integral theorem, the contribution to the interaction containing all terms linear in $\tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega)$ can now be evaluated as

$$\begin{aligned} H_{ia}^\eta(\omega) = & \frac{i}{\omega} \int d\mathbf{r} \\ & \times \left[(\nabla \times \mathbf{v}_{ia}(\mathbf{r})) \cdot \tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega) (\nabla \times \mathbf{u}(\mathbf{r}, \omega)) \right. \\ & + \frac{4}{3} (\nabla \cdot \mathbf{v}_{ia}(\mathbf{r})) \tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega) (\nabla \cdot \mathbf{u}(\mathbf{r}, \omega)) \\ & + 2 (\nabla \cdot \mathbf{v}_{ia}(\mathbf{r})) \nabla \tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega) \cdot \mathbf{u}(\mathbf{r}, \omega) \\ & + 2 \mathbf{v}_{ia}(\mathbf{r}) \cdot \nabla \nabla \tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega) \cdot \mathbf{u}(\mathbf{r}, \omega) \\ & \left. + 2 \mathbf{v}_{ia}(\mathbf{r}) \cdot \nabla \tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega) (\nabla \cdot \mathbf{u}(\mathbf{r}, \omega)) \right]. \end{aligned} \quad (28)$$

Similarly for the terms linear in $\tilde{\zeta}_{xc}(\rho_0(\mathbf{r}), \omega)$ we obtain

$$H_{ia}^\zeta(\omega) = \frac{i}{\omega} \int (\nabla \cdot \mathbf{v}_{ia}(\mathbf{r})) \tilde{\zeta}_{xc}(\rho_0(\mathbf{r}), \omega) (\nabla \cdot \mathbf{u}(\mathbf{r}, \omega)) d\mathbf{r}. \quad (29)$$

From these expressions we see that we only need to evaluate the velocity fields \mathbf{v}_{ia} and \mathbf{u} as well as their divergence and curl. Moreover we need to calculate the first and

second derivatives of the functions $\tilde{\eta}_{xc}(\rho_0(\mathbf{r}), \omega)$ and $\tilde{\xi}_{xc}(\rho_0(\mathbf{r}), \omega)$. Since they are simple functions of the density these derivatives can be evaluated once we know the first and second derivatives of the ground state density. We obtain the following equations for the divergence and curl of \mathbf{v}_{ia} :

$$\nabla \cdot \mathbf{v}_{ia}(\mathbf{r}) = \frac{1}{\rho_0(\mathbf{r})} \left(i(\epsilon_i - \epsilon_a) \phi_a^*(\mathbf{r}) \phi_i(\mathbf{r}) - \frac{\nabla \rho_0(\mathbf{r})}{\rho_0(\mathbf{r})} \cdot \mathbf{j}_{ia}(\mathbf{r}) \right), \quad (30)$$

$$\nabla \times \mathbf{v}_{ia}(\mathbf{r}) = \frac{1}{\rho_0(\mathbf{r})} \left(-i \nabla \phi_a^*(\mathbf{r}) \times \nabla \phi_i(\mathbf{r}) - \frac{\nabla \rho_0(\mathbf{r})}{\rho_0(\mathbf{r})} \times \mathbf{j}_{ia}(\mathbf{r}) \right), \quad (31)$$

where we have explicitly used that the orbitals are eigenstates of the ground state Kohn–Sham Hamiltonian. These expressions only involve first order derivatives of the orbitals. For the divergence and curl of \mathbf{u} we obtain

$$\nabla \cdot \mathbf{u}(\mathbf{r}, \omega) = \frac{1}{\rho_0(\mathbf{r})} \left(i \omega \delta \rho(\mathbf{r}, \omega) - \frac{\nabla \rho_0(\mathbf{r})}{\rho_0(\mathbf{r})} \cdot \delta \mathbf{j}(\mathbf{r}, \omega) \right), \quad (32)$$

$$\nabla \times \mathbf{u}(\mathbf{r}, \omega) = \frac{1}{\rho_0(\mathbf{r})} \left(\delta \mathbf{m}(\mathbf{r}, \omega) + \delta \mathbf{j}(\mathbf{r}, \omega) \times \frac{\nabla \rho_0(\mathbf{r})}{\rho_0(\mathbf{r})} \right), \quad (33)$$

where we used the continuity equation to relate the divergence of the induced current to the induced density,

$$\nabla \cdot \delta \mathbf{j}(\mathbf{r}, \omega) - i \omega \delta \rho(\mathbf{r}, \omega) = 0, \quad (34)$$

and where the curl of the current, $\delta \mathbf{m}(\mathbf{r}, \omega) = \nabla \times \delta \mathbf{j}(\mathbf{r}, \omega)$, is obtained from an equation similar to Eq. (12),

$$\delta \mathbf{m}(\mathbf{r}, \omega) = \int \left(\{ \chi_{\mathbf{m}\mathbf{j}}^s(\mathbf{r}, \mathbf{r}', \omega) - \chi_{\mathbf{m}\mathbf{j}}^s(\mathbf{r}, \mathbf{r}', 0) \} \cdot \delta \mathbf{A}_{\text{eff}}(\mathbf{r}', \omega) + \chi_{\mathbf{m}\rho}^s(\mathbf{r}, \mathbf{r}', \omega) \times \delta v_{\text{eff}}(\mathbf{r}', \omega) \right) d\mathbf{r}'. \quad (35)$$

Here the response functions $\chi_{\mathbf{m}\mathbf{j}}^s(\mathbf{r}, \omega)$ and $\chi_{\mathbf{m}\rho}^s(\mathbf{r}, \omega)$ can be obtained from Eq. (14) by substituting the operator $\hat{\mathbf{m}} = -i(\nabla^\dagger \times \nabla)$. From the previous discussion we see that we can evaluate the matrix elements of the VK functional once we have the induced density $\delta \rho$, the induced current $\delta \mathbf{j}$, and its curl $\delta \mathbf{m}$. Equations (11), (12), and (35) become a coupled set. Note that in this way we have avoided the explicit evaluation of orbital derivatives higher than first order. By including the ALDA in the scalar potential instead of in the vector potential we also avoid evaluation of the gradient of $\delta \rho$ and conform to standard implementations of TDDFT.

The transverse and longitudinal response kernels $f_{xcL}(\omega)$ and $f_{xcT}(\omega)$ have been investigated for the electron gas.^{35–38} They are smooth functions for small frequencies.³⁹ In the limit $\omega \rightarrow 0$ the contribution of $f_{xcL}(\omega)$ drops out identically. In order to implement the VK functional in this limit we only need to obtain the values of the exchange correlation kernel $f_{xcT}(0)$ as a function of ρ_0 . To obtain values for

TABLE I. The axial polarizabilities per oligomer unit in atomic units (a.u.) of the monomer and dimer of PDA and PBT at different levels of theory.

		ALDA	VK	HF ^a	CCSD(T) ^b
PDA	monomer	78.71	67.32	66.71	65.03
	dimer	129.13	94.30	97.36	92.5
PBT	monomer	102.94	85.21	100.31	92.06
	dimer	172.96	117.13	162.19	136.1

^aReference 52.

^bReference 62.

$f_{xcT}(0)$ at arbitrary ρ_0 , Eq. (19) of Ref. 36 is used together with the values in Table I of the same reference. In this table the exchange correlation kernel is only given at certain $r_s (4\pi r_s^3/3 = 1/\rho_0)$ values. Not all values of this table can be used, only the values for $r_s \leq 5$ are realistic. To obtain the values for $f_{xcT}(0)$ a cubic spline interpolation has been used in the range 0–5 for the r_s values, where the exact quadratic behavior for small r_s is taken into account.³⁸ For values $r_s > 5$ we keep $f_{xcT}(0)$ constant and equal to its value at $r_s = 5$. We checked that changing the behavior of $f_{xcT}(0)$ for $r_s > 5$ did not influence our results. In Fig. 1 the values for $f_{xcT}(0)$ are plotted against r_s for $r_s \leq 5$.

Within the ADF the exact ground state density, expressed as one and two-center products of basis functions, is represented by an expansion in one-center functions only.⁴⁷ This is done to facilitate the calculation of the Coulomb potential, but also to evaluate the first and second order derivatives of the density. A drawback, however, is that this fitted density can become zero or negative, which is unphysical. This poses problems for the evaluation of terms of the form, $\nabla \rho_0 / \rho_0$ and $\nabla \nabla \rho_0 / \rho_0$. To prevent this problem, the absolute value of the fitted density is used and a small offset is introduced. The fitted density is replaced by $\rho_0^{\text{safe}} = |\rho_0^{\text{fit}}| + \Delta$, where $\Delta = 1.0 \cdot 10^{-3}$. We checked that the value of Δ did not have any notable influence on the results while ensuring the stability of the calculation.

The external electric field in our implementation of the response equations is expressed as $\mathbf{E}_{\text{ext}}(\omega) = -i\omega \hat{\mathbf{e}}_j$. One

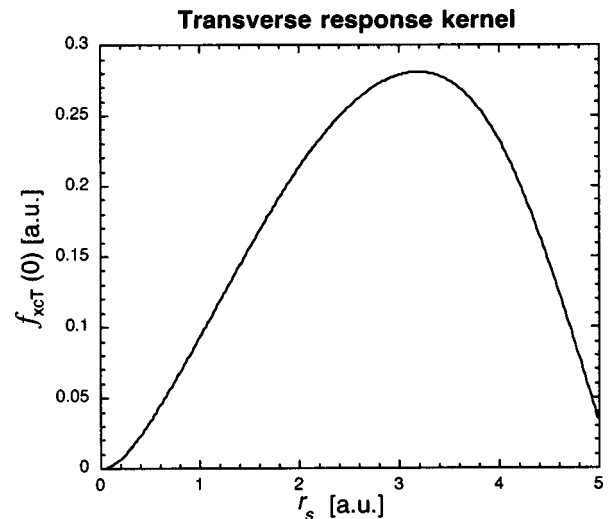


FIG. 1. Values of the transverse response kernel $f_{xcT}(0)$ for values of $r_s \leq 5$.

then obtains the following expression for the polarizability tensor:

$$\alpha_{ij}(\omega) = \left\{ \frac{-1}{\omega} \int \delta j_i(\mathbf{r}, \omega) d\mathbf{r} \right\}_{\mathbf{E}(\omega) = -i\omega \hat{\mathbf{e}}_j} \quad (36)$$

We calculate the polarizability at several frequencies close to zero and extrapolate the result to the static limit.

IV. COMPUTATIONAL DETAILS

All calculations were performed with our modified version of ADF.^{40–45} In these calculations we used the standard ADF basis set V, which is a triple zeta Slater-type basis set augmented with two polarization functions. Cores were kept frozen for carbon and nitrogen up to 1s and the silicon core up to 2p. These basis sets are sufficiently large for our purpose of comparison. All integrals have been evaluated with at least three significant figures. The ground state has been calculated with the LDA functional in the VWN parameterization.⁴⁸

We compare our VK results to other existing (*ab initio*) calculations from the literature. Therefore we attempted in all cases to use a geometry equal or at least very close to the geometries used in the reference calculations. In each case we used a fixed monomer geometry for all oligomers of a specific type. These monomer geometries are equal to the converged geometries (with respect to chain length) from the references. Note that in some references geometries have been optimized per oligomer. The monomer geometries we used are depicted in the insets of Figs. 2–6 for polyethylene (PE),⁴⁹ polysilane (PSi),⁴⁹ polysilene (PSi2),⁵⁰ polymethineimine (PMI),⁵¹ and polybutatriene (PBT).⁵² For computational details and results on the systems, polyacetylene (PA), polydiacetylene (PDA), polyyne (PY), polythiophene (PT) and the hydrogen chain model, we refer to Ref. 6. The polymethineimine geometry was obtained from Ref. 51, where we used their type A *trans*-transoid polymethineimine geometry for the monomer. The PSi2 geometry was obtained from Ref. 50, where we chose the geometry of the central units and a value of 1.500 Å for the Si–H bond length. The equilibrium bond length of the diatomic silyldiyne molecule (HSi) is 1.5201 Å,⁵³ the Si–H bond length in several other silicon compounds is about 1.48 Å.⁵³ The polarizability differs less than 0.5% by changing the Si–H distance from 1.500 to 1.480 Å.

The axial polarizability per oligomer unit can be obtained with several methods, for example by simply dividing the axial polarizability by the number of units or by subtracting the polarizability of the oligomer with $N-1$ units from that with N units. The results for these methods are not identical. We divided the axial polarizability by the number of units. In cases from literature where originally other methods were used, the results were recalculated to be in accordance with our method.

V. RESULTS

In a previous paper⁶ we studied polyacetylene (PA), one of the prototypes of the π -conjugated oligomers. We showed that the VK results are close to the best available results

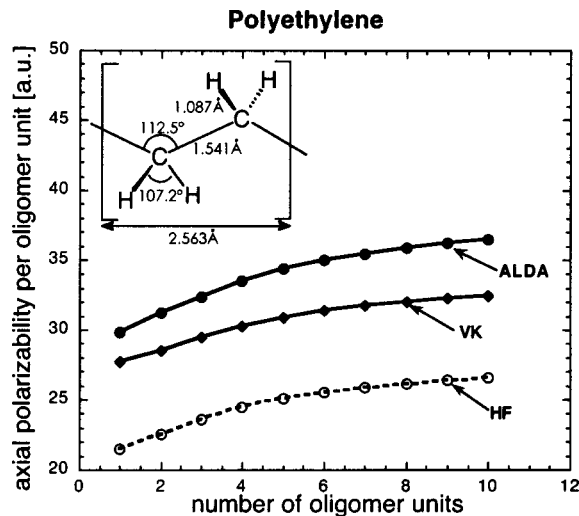


FIG. 2. ALDA and VK static axial polarizability of polyethylene compared with coupled HF (Ref. 49) results.

obtained with Møller–Plesset second order perturbation theory (MP2).⁵⁴ The same was observed for the other conjugated systems polyyne (PY), polythiophene (PT), and polydiacetylene (PDA). The VK functional thus seems to have an important effect for conjugated systems. The classical interpretation of conjugation is that there is a special distinction between delocalized systems of electrons in conjugated molecules and localized two center bonds in nonconjugated molecules.⁵⁵ However, more important for the behavior of the polarization of polymers is not the conjugation but the electron delocalization or mobility, which is measured by the polarizability.

To study the effect of conjugation we first study polyethylene (PE), a system that is generally considered to be nonconjugated. As examples of conjugated oligomers we discuss the σ -conjugated polysilane (PSi) and π -conjugated polysilene (PSi2) and polymethineimine (PMI). We have discussed PDA in Ref. 6. Here we will discuss its tautomer polybutatriene (PBT) for which large differences in polarizability have been found with the Hartree–Fock (HF) method. Finally we discuss the hydrogen chain model for which VK only shows small improvements.

We studied polyethylene (PE) in its linear zig–zag form. The ALDA and VK results are depicted in Fig. 2 and compared with coupled perturbed Hartree–Fock (CPHF) 3-21G results.⁴⁹ Unlike in the case of conjugated polymers we see that ALDA, VK, and HF curves run almost parallel. Remarkable is that ALDA does not give a large overestimation of the polarizability for the longer oligomers. VK only gives a small and reasonably constant correction to the ALDA results. The experimental average polarizability for the monomer is 29.62 a.u.⁵⁶ This is close to the ALDA result with a very large basis set [30.74 a.u. (Ref. 57)]. Our VK value for the average polarizability of the monomer is 26.69 a.u. These values for the average polarizability are already considerably larger than the HF value of 21.49 a.u. Polarizabilities obtained with more accurate methods are therefore expected to be closer to the experimental as well as ALDA and VK values. Since VK gives a small correction on the ALDA, appar-

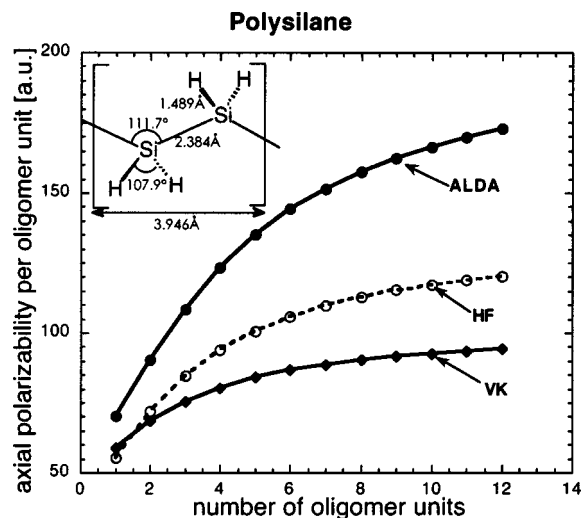


FIG. 3. ALDA and VK static axial polarizability of polysilane compared with coupled HF (Ref. 49) results.

ently nonlocal effects described by VK are not important in this system. This is consistent with low electron mobility in PE. The silicon analog of PE is polysilane (PSi). Unlike in PE there is experimental and theoretical evidence for σ -conjugation in PSi (see, for example, Refs. 49 and 50, and references therein). Our results are displayed in Fig. 3. The polarizability per unit increases more steeply with chain length for ALDA than for HF, although the overestimation is not as severe as in the π -conjugated systems. In contrast to what we observed for PE, VK gives a large correction in PSi, which brings the results closer to the available CPHF results.⁴⁹ Apparently nonlocal effects described by VK are important for this system.

The silicon analog of PA is polysilene (PSi₂). Because PSi already has a high polarizability the PSi₂ molecule is expected to be even more polarizable. CPHF calculations confirm this assertion.⁵⁰ In Fig. 4 these HF results are compared with our ALDA and VK results. As expected the ALDA strongly overestimates the polarizability per unit and

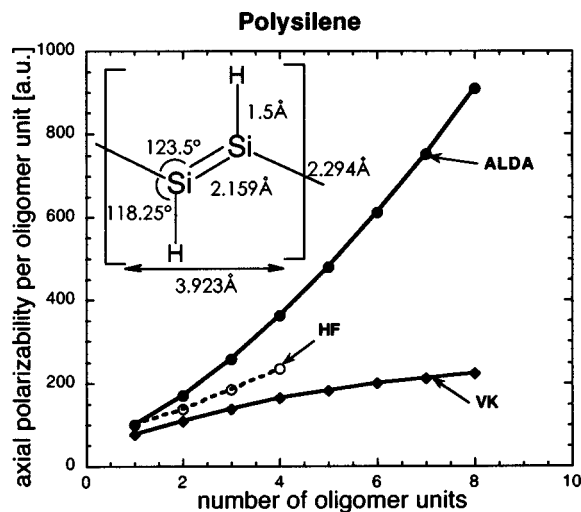


FIG. 4. ALDA and VK static axial polarizability of polysilene compared with coupled HF (Ref. 50) results.

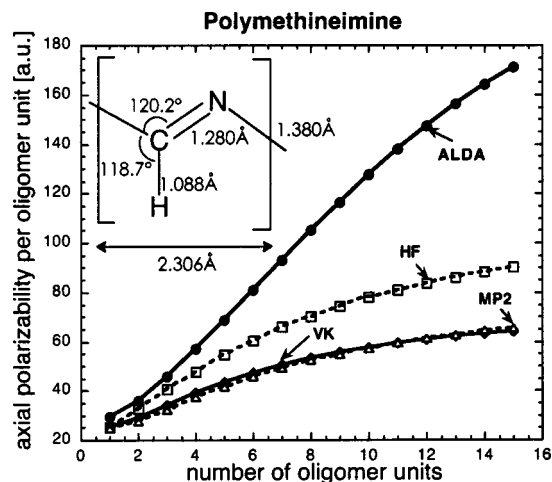


FIG. 5. ALDA and VK static axial polarizability of polymethineimine compared with coupled HF (Ref. 51) and MP2 (Ref. 58) results.

increases steeply with chain length (more than linearly). In this case VK drastically modifies the results, which is indicative of very large nonlocal effects. Going from PE, via PA and PSi, to PSi₂ we see an increase in the polarizability. Within this series we also observe the trend that the ALDA overestimation increases and the VK corrections become larger. It therefore seems that high electron mobility and nonlocal effects are connected.

A system that is isoelectronic with PA is polymethineimine (PMI). Our ALDA and VK results are depicted in Fig. 5 and compared with CPHF 6-31G results,⁵¹ we also compare to MP2 6-31G results with a slightly different geometry.⁵⁸ The VK results are on top of these MP2 results and give a large correction to ALDA. This is very similar to the results we observed for PA.

The MP2 results were obtained with a somewhat different geometry, namely the type B geometry from Ref. 51. We did calculations on PMI oligomers of the type B geometry with 5 and 10 units and found a reduction in the axial polarizability of 3.9% and 5.7%, respectively, compared to type A. In case of HF the changes are larger, with percentages of 8.1% and 12.8%, respectively. This shows that, at least for this system, VK is less sensitive to geometry changes than HF. From this we conclude that it is justified to compare our VK results with the MP2 results.

Systems in which HF is even more sensitive to the geometry, whereas VK is not, are the polydiacetylenes. Depending on the nature of their sidegroups, polydiacetylenes can occur in a structure ranging from the acetylenic $[\text{CR}=\text{CR}'-\text{C}\equiv\text{C}]_N$ to the butatrienic $[\text{CR}=\text{C}=\text{C}=\text{CR}']_N$ form. PDA and polybutatriene (PBT) with $\text{R}=\text{R}'=\text{H}$ are interesting systems to compare. These systems are tautomers of which PDA turns out to be the stable configuration. We already discussed PDA in Ref. 6. Here we present results for PBT. In Fig. 6 we compare our ALDA and VK results for PBT with CPHF 6-31G results.⁵² The ALDA results again severely overestimate the polarizability. Again VK gives a huge reduction of this polarizability but the results are much smaller than the HF results.

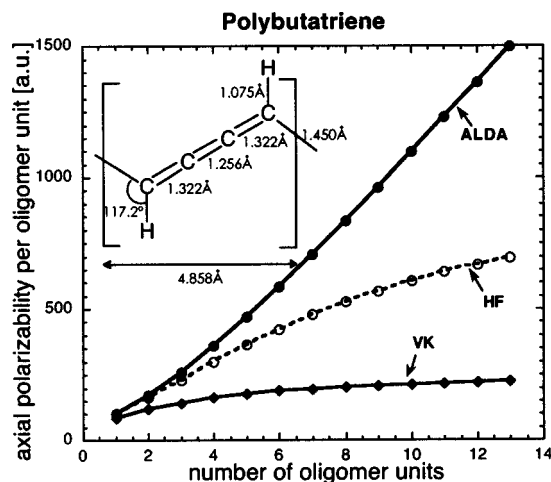


FIG. 6. ALDA and VK static axial polarizability of polybutatriene compared with coupled HF (Ref. 52) results.

Apparently the ultranonlocal effects treated by VK are very important in this system.

The difference between the axial polarizabilities for VK and HF in PBT is very different from what we observed for PDA, where the VK and HF results are in close agreement. In Fig. 7 the results for PDA and PBT are compared for VK and HF.⁵² The VK results for PBT and PDA are very similar, the values for PBT being somewhat bigger. Note that the HF results for PBT give a surprisingly large value for the axial polarizability compared with the HF results for PDA. The disagreement between HF and VK for PBT raises the question which method gives the most accurate results. Other HF results are available for infinite chains⁵⁹ and for the average polarizability of small oligomers.⁶⁰ Champagne and Öhrn⁵⁹ did CPHF calculations on the infinite PDA and PBT systems. The values for the axial polarizability per oligomer unit are 134.4 a.u. for PDA and 626.4 a.u. for PBT with HF using the minimal STO-3G basis. Again the PBT value is much higher than the PDA value. These values are smaller than found by Perpète *et al.*⁵² for the longer oligomers. It should be noted that the infinite chain calculations were done in a minimal

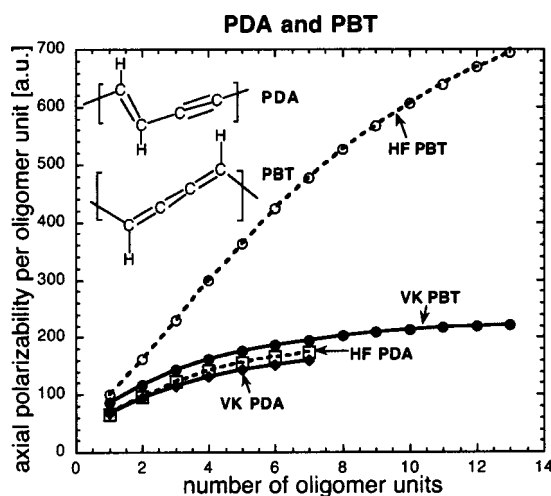


FIG. 7. Results for the static axial polarizability of polydiacetylene and polybutatriene are compared for VK and coupled HF (Ref. 52).

STO-3G basis set. These results are in disagreement with the results for PBT of Bodart *et al.*⁶⁰ for the average polarizability $\langle\alpha\rangle=(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$, obtained with finite-field HF within the minimal STO-3G basis set. Since for these polymeric systems the dominant contribution to the average polarizability is in the axial direction, we may compare these values with the value for the axial polarizability. The value of the average polarizability we obtained with VK (63.49 a.u. per unit) for the three unit oligomer agrees with their value (61.61 a.u. per unit). Accurate benchmark results^{61,62} obtained with the coupled-cluster (CCSD(T)) method in a double zeta basis set with one polarization function, are available for the monomer and dimer of PDA and PBT in the same geometry as used by us. These results are presented in Table I. From this table it is clear that the PDA results for VK, CPHF, and CCSD(T) are close to each other. Much larger differences are found for the PBT case, where the CCSD(T) values are in between the HF and VK values. Unfortunately no accurate results are available for the longer oligomers. This does not allow us to make further conclusions on the accuracy of the VK versus HF results in case of PBT. No direct experimental results are available for this system. Perpète *et al.*⁵² estimated the polarizabilities of PDA and PBT using the experimental values for the polydiacetylenes PTS ($R=R'=\text{CH}_2-\text{O}=\text{SO}_2-\text{C}_6\text{H}_4-\text{CH}_3$) and TDCU ($R=R'=(\text{CH}_2)_4-\text{O}-\text{CO}-\text{NH}-\text{C}_6\text{H}_5$). They derived a value of 383 a.u. for PDA and 402 a.u. for PBT for the axial polarizability per oligomer unit for infinite chains. These values indicate that the PBT values are only slightly bigger than the PDA results. They are in the same range as our VK results and much smaller than the HF results for PBT. More insight in this issue can be obtained from accurate correlated *ab initio* methods applied to longer oligomers, which leaves an interesting future challenge.

A clear picture emerges from the systems studied so far. For all systems where ALDA overestimates the polarizability, the VK correction is large. For the systems PA and PMI where MP2 results are available we see that VK is in excellent agreement. For these cases we also observe that the MP2 values give a large correction on available HF results. The general trend observed in hydrocarbons, is that the static polarizability decreases as one goes beyond the HF approximation.^{13,54,63} We find the same trend for VK in relation to HF, which may indicate that the VK results are in general close to MP2.

An important exception to this observation seems to be the hydrogen chain model, H_{2n} .⁶ In this system the ALDA overestimates the polarizability considerably and VK gives only a slight correction. This calls for an explanation. We observe that the induced current is too large since the same is true for the VK polarizability. Hence the counteracting xc-electric field that is introduced by VK is not large enough to get the correct polarizability as obtained from CCSD(T) and MP4. From Eq. (18) we see that the counteracting field is proportional to the induced current. If the VK is able to incorporate all nonlocal effects then we can conclude that the proportionality coefficient $f_{xc}(0)$ is too small for this system. To investigate the dependence of VK on the size of the

TABLE II. Exponents ζ for the hydrogen chain model H_{2n} with different bond length alternations (BLAs). Exponents are calculated from the values found in the figure in Ref. 6. Here ALDA-VK denotes the difference between the ALDA and VK exponents.

BLA (a.u.)	ALDA	VK	ALDA-VK	CHF	MP4	CCSD(T)
0	2.37	2.12	0.25			
0.5	1.73	1.66	0.07	1.49	1.50	1.48
2	1.17	1.16	0.01	1.10	1.09	1.09

induced current we study hydrogen chain models by varying the bond length alternation (BLA). By increasing the bond-length alternation of the hydrogen chain, the system ranges from a metallic one-dimensional chain (BLA=0) to a Peierls distorted semiconductor or insulator (BLA \gg 1). For the case BLA=0 we expect large induced currents and hence a large counteracting field. However, even in this case we only found a reduction in the order of 30% for 15 H_2 units. We suggest two possible reasons for the failure of VK for hydrogen chain model. It is possible that the VK functional has the right form but that the density behavior of the coefficients is insufficient. On the other hand, it could be that the form of the VK functional is too restricted to treat all xc-effects that affect the polarizability.

VI. DISCUSSION

Until now we have discussed all systems separately. For the purpose of an overall comparison of the performance of the VK functional, it is desirable to classify the systems according to their polarizability. We found that the polarizability as a function of the chain length can be very well described by the following power law:

$$\alpha(N) = AN^\zeta, \quad (1 \leq \zeta \leq 3), \quad (37)$$

where N is the number of monomer units. The same power law has been used before in the fitting of the polarizability of oligomer chains.⁵⁰ We determined the exponent by a least squares fitting procedure to a straight line for a log-log plot, thereby weighing the N th data point by N . This power law has been derived on the basis of Hückel,^{64,65} electron gas,⁶⁶ and Hubbard models.⁶⁷ The exponent $\zeta=3$ corresponds to the limit of free electrons on a rod, whereas the exponent $\zeta=1$ is derived for a Hubbard model with infinite on-site repulsion, i.e., the limit of localized electrons. We can therefore consider the parameter ζ as a measure for the degree of delocalization, and order the systems accordingly. Of course our molecules differ from these idealized model systems and one may argue that for example an offset is needed to account for the endgroups. We do not expect that such modifications of the power law will substantially change the value found for the exponents, especially since endgroup effects become small for the long chains.

As a first example we can look at the hydrogen chain model with different BLAs. The exponents we found are presented in Table II. For BLA=0 we find a value of $\zeta=2.37$ for the ALDA, which is close to the free electron limit. For the other extreme, BLA=2, we find $\zeta=1.17$ for the ALDA, which is close to the limit of localized electrons. For the

TABLE III. Exponents ζ for various oligomers. Exponents are calculated from the values found in the figures in this article and in Ref. 6. Here ALDA-VK denotes the difference between the ALDA and VK exponents.

System	ALDA	VK	ALDA-VK	HF	MP2/SOPPA ^a
PE	1.09	1.07	0.02	1.09	
PSi	1.31	1.14	0.17	1.23	
PY	1.75	1.50	0.25	1.41	1.43
PA	1.94	1.41	0.53	1.52	1.52
PMI	1.81	1.35	0.46	1.36	1.39
PT	1.76	1.39	0.37	1.44	
PDA	1.85	1.40	0.45	1.43	
PBT	2.19	1.27	0.92	1.70	
PSi2	2.23	1.48	0.75	1.68 ^b	

^aMP2 results for PA and PMI, SOPPA results for PY.

^bThis value is based on only 4 data points.

hydrogen chain model the VK turns out to reduce this exponent only slightly. It is clear that, at least for BLA=0.5 and BLA=2, the VK is unable to introduce a sufficient amount of localization in H_{2n} . The HF exponents, on the other hand, agree well with MP4 and CCSD(T).

In Table III we give the exponents for the other systems studied here and in previous work,⁶ together with the values obtained from the cited reference data. We observe that VK in general gives a reduction of the exponent in agreement with the HF values, except for PBT and PSi2. Note, however, that for PSi2 the HF exponent is only based on 4 data points. Where comparative data are available, both the VK and HF exponents are in good agreement with correlated wave function methods. The HF values for the polarizability itself are, however, larger than those of the correlated methods due to a larger prefactor A in Eq. (37).

Earlier we observed the trend in the polarizabilities in going from PE, via PA and PSi, to PSi2, that the ALDA overestimation increases and the VK correction becomes larger. However the exponents reveal that with growing chain length the PA chains will ultimately be more polarizable than the PSi chains. In view of this, the correct order for the polarizability in the very long chain limit should be PE-PSi-PA-PSi2. The same order is observed as we look at the reduction of the ALDA exponents by VK. According to our definition of localization by means of the exponents of the power law, we can state that the electron delocalization is most prominent in PSi2 and nearly absent in PE, which is in accordance with intuitive views.

In summary we can say that the ALDA exponents are more reduced by the VK if they are larger. The VK exponents are in good agreement with HF methods and beyond, except for the hydrogen chain model.

VII. CONCLUSIONS

We have applied TDCDFT to a range of finite oligomers. By treating the xc-effects using the current functional derived by Vignale and Kohn we were able to obtain polarizabilities in good agreement with accurate wave function methods. The VK functional achieves large corrections to the ALDA that was known to overestimate the polarizability considerably for conjugated oligomers. Moreover the large N behavior of VK as described by a power law was found to be

in good agreement with reference data. For the hydrogen chain model we indicated that further improvements are probably needed in the VK functional, in particular with regard to the density dependence of $f_{xcT}(0)$.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Denis Jacquemin and Benoît Champagne for providing us with their unpublished MP2 data on the polarizabilities of PMI. We also thank Tobita Motoi, So Hirata, and Rodney J. Bartlett for many useful discussions and providing us with benchmark CCSD(T) data on PBT.

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